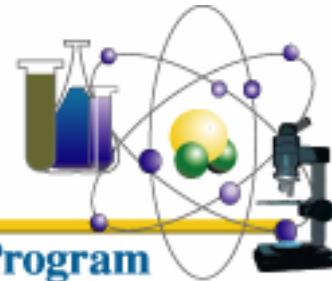




EMSP

Environmental Management Science Program



Project No. 81935

Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts

*Bruce A. Moyer,¹ Peter V. Bonnesen,¹ Lætitia H. Delmau,¹
Nancy L. Engle,¹ Tamara J. Haverlock,¹ Hyun-Ah Kang,¹
Tatiana G. Levitskaia,² Gregg J. Lumetta²*

- ¹ Oak Ridge National Laboratory
- ² Pacific Northwest National Laboratory

EMSP High-Level Waste Workshop
Savannah River National Laboratory
Jan. 19 and 20, 2005

Contact information

Bruce A. Moyer and Peter V. Bonnesen*

Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6119. Phone: 865-574-6718. Fax: 865-574-4939. Email: moyerba@ornl.gov

Tatiana G. Levitskaia and Gregg J. Lumetta*

Radiochemical Science and Engineering Group, Pacific Northwest National Laboratory, P.O. Box 999, MSIN P7-22, Richland, WA 99352. Phone: 509-376-8242. Fax: 509-373-9675. Email: Tatiana.Levitskaia@pnl.gov

**Site Principal Investigator. ORNL is lead institution.*

We gratefully acknowledge our former collaboration with Prof. Alan P. Marchand (ret.), Univ. of North Texas.

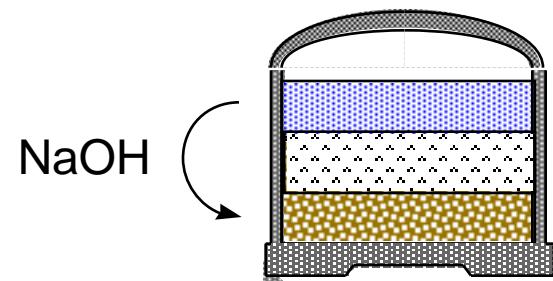
The purpose of this project is to explore new liquid-liquid extraction approaches to the separation of sodium hydroxide and sodium salts from alkaline tank waste.

Objectives:

- Ø **Develop concept of pseudo hydroxide extraction for NaOH**
 - Identify weakly acidic cation exchangers
 - Explore extraction behavior and develop comprehensive model
- Ø **Explore systems involving macrocyclic extractants**
 - Establish feasibility of NaX (esp. NaNO_3) extraction
 - Develop concept of synergistic pseudo hydroxide extraction (SPHE)
 - Determine efficacy of ionizable lariat ethers
- Ø **Investigate applicability in simple tests with real tank waste**

Sodium separation from LAW yields potential savings

Possible benefits:



Reduced low-activity-waste (LAW) glass production

- Divert sodium to alternative waste form, such as grout
- Accelerated waste processing (mission acceleration)

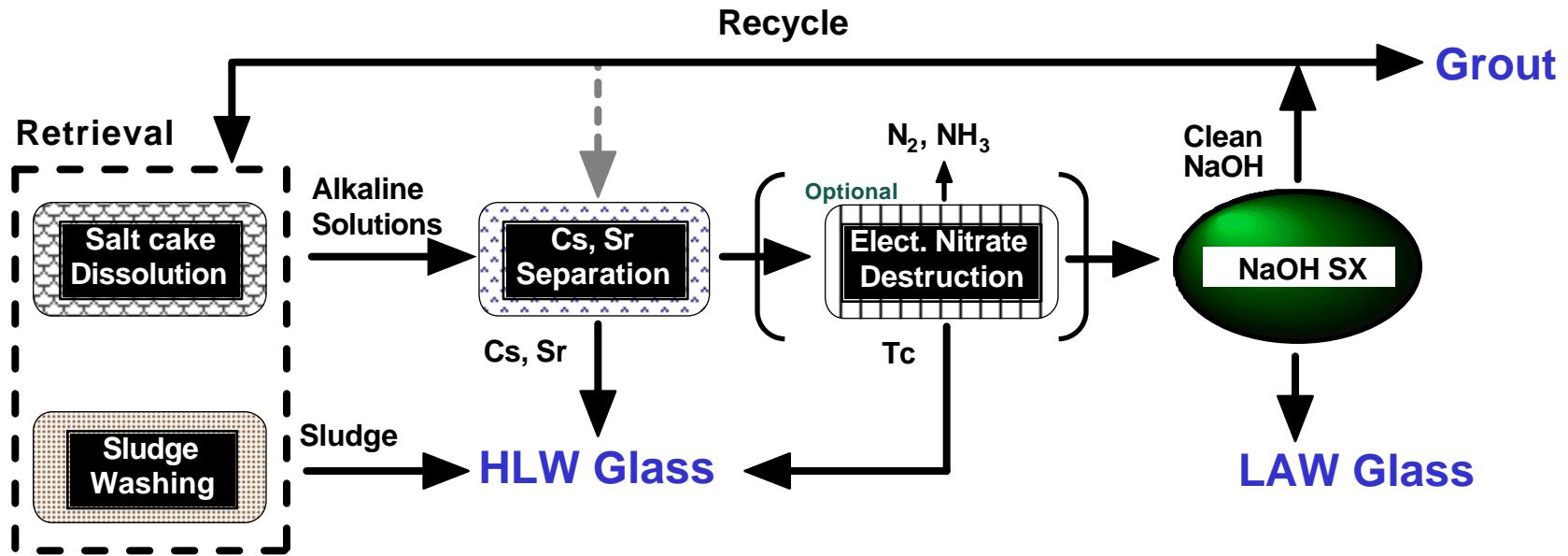
NaOH recycle for retrieval, sludge washing, etc.

- Reduces or eliminates addition of NaOH
- Reduced retrieval risk

Avoidance of new tank construction

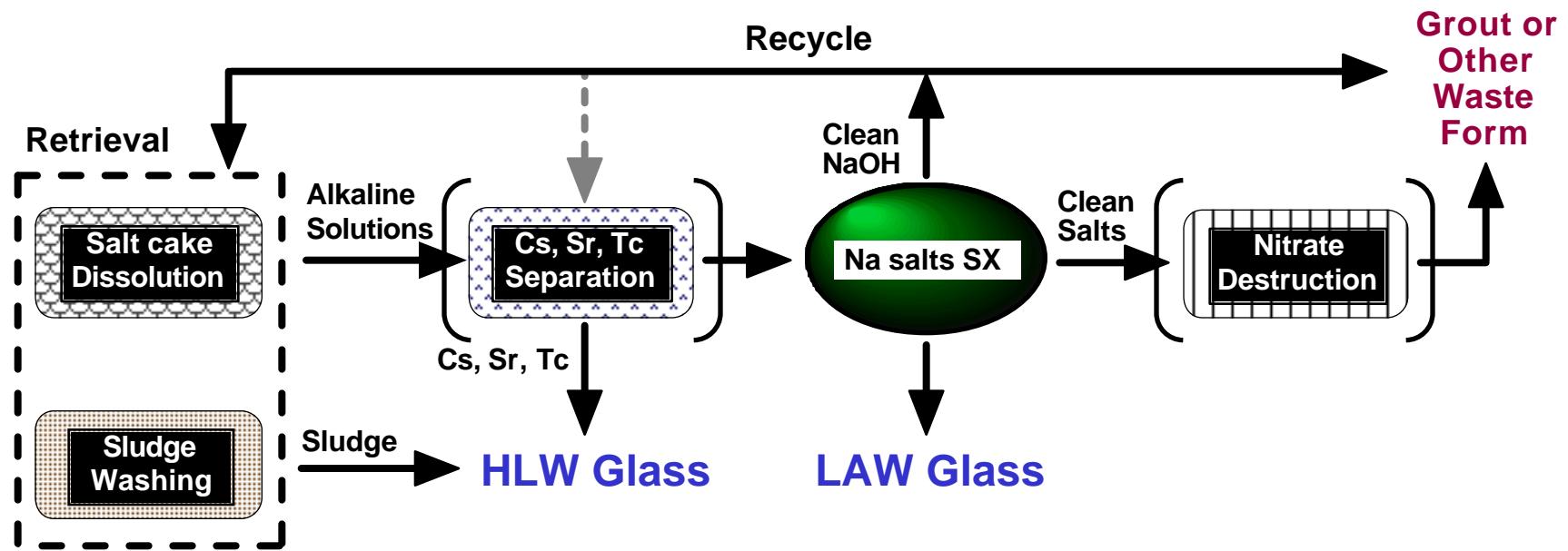
- Waste debulking on skid-mounted units

Clean sodium concept using NaOH solvent extraction (SX)



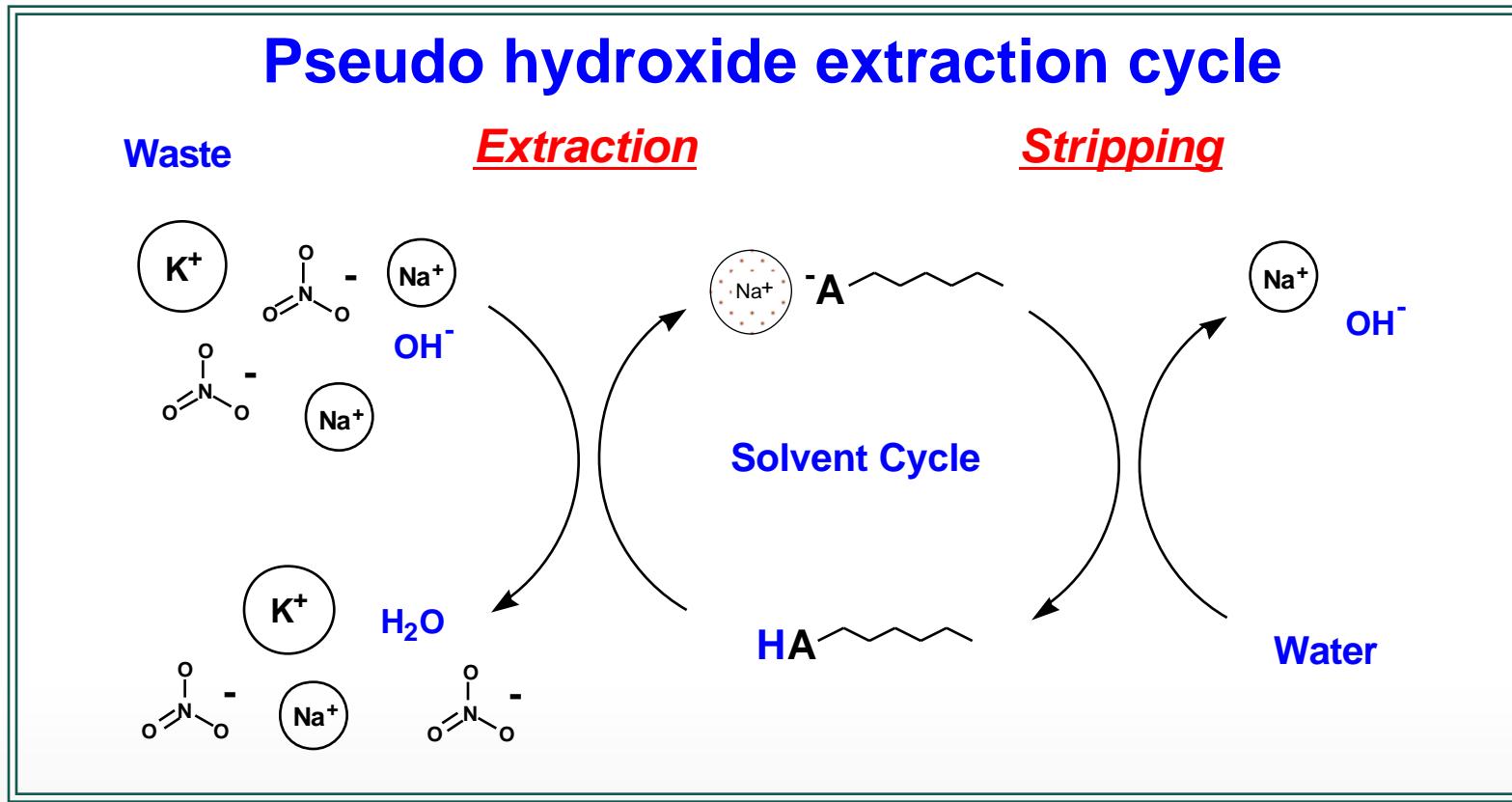
Note! This is a speculative flowsheet for discussion.

Clean sodium concept using near-total NaX extraction



Note! This is a speculative flowsheet for discussion.

A simple, economical approach to NaOH separation has been developed using cation exchange

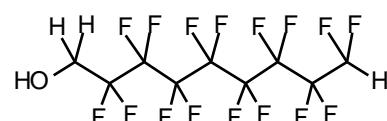


B. A. Moyer, C. K. Chambliss, P. V. Bonnesen, and T. J. Keever, **Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures**, U.S. Patent 6,322,702, Nov. 27, 2001.

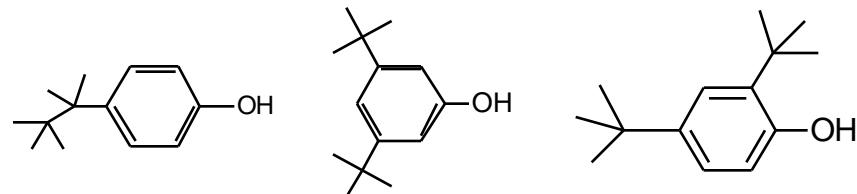
Weakly acidic cation exchangers studied

Major classes and examples:

Linear fluorinated alkanols

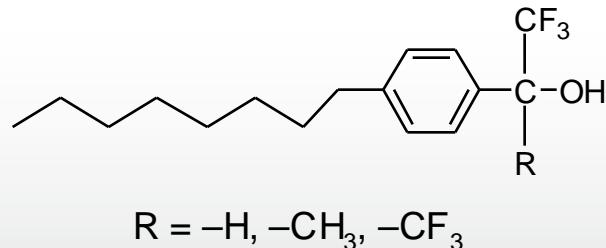


Alkyl phenols

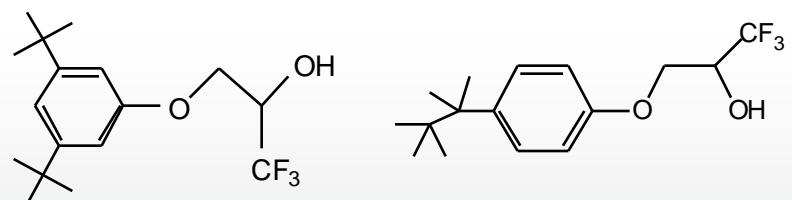


Alcohols with -CF₃ substituents:

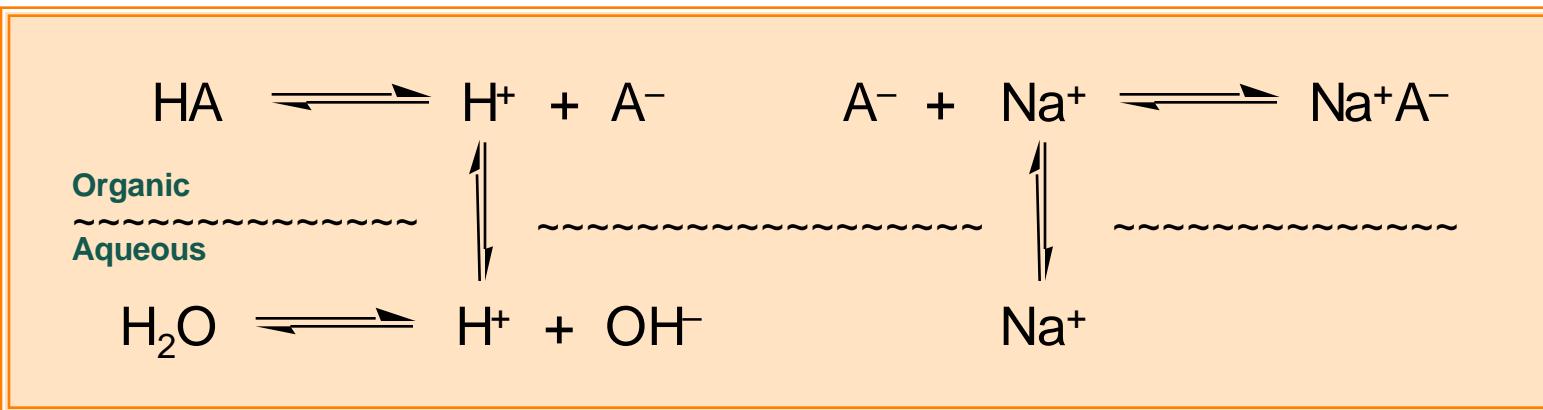
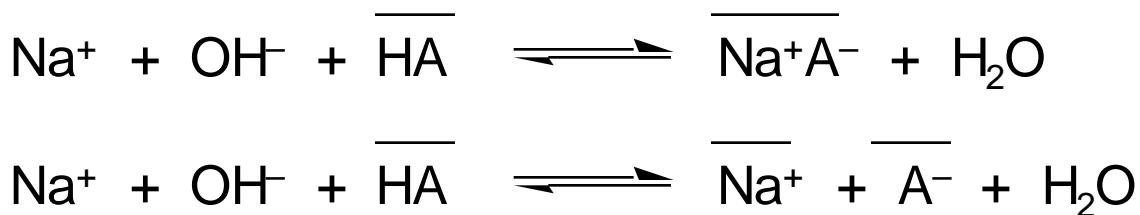
Alkyl benzyl alcohols



Alkyl phenoxy ethanols

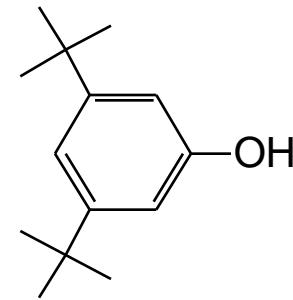
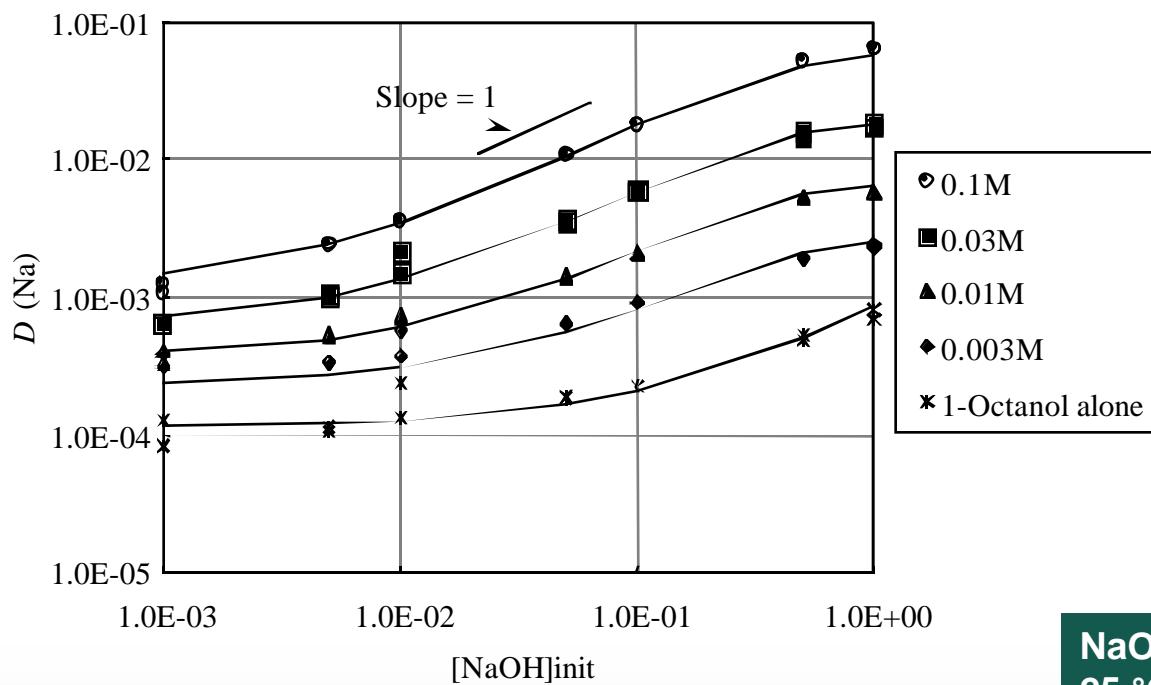


A simple model based on cation exchange nicely explains pseudo hydroxide extraction



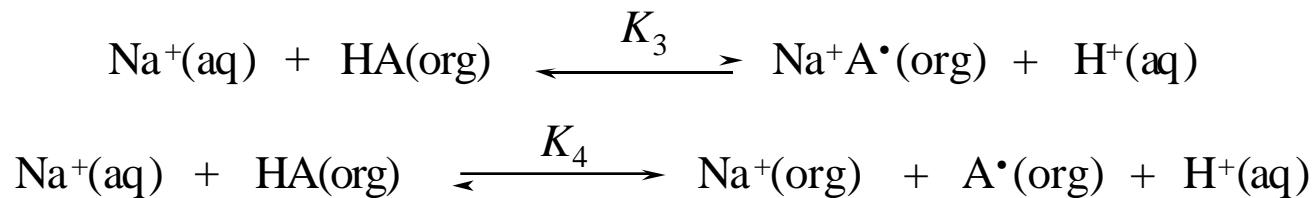
Conversion to phenoxide or alkoxide confirmed by FTIR and Raman spectroscopy. L. Maya, B. A. Moyer, and M. J. Lance *Appl. Spectrosc.* **2003**, 57, 238–241.

Cation-exchange model fits data

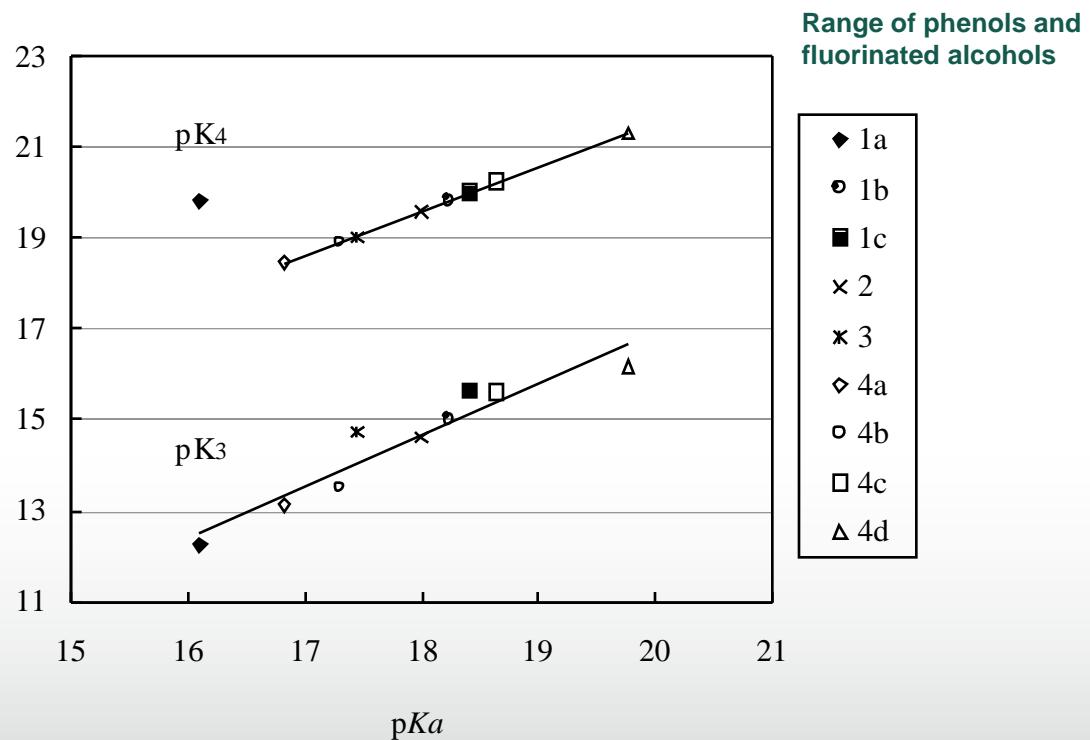


NaOH extraction isotherms
25 °C; O/A = 3
1-octanol diluent
NaOH only aqueous electrolyte

PHE strength correlates with acidity of cation exchanger



Values of pK for extraction plotted vs. pK_a in water-saturated 1-octanol



Future efforts on pseudo hydroxide extraction

Complete equilibrium model

- Relate extraction strength to pK_a of cation exchanger
- Correlate pK_a to physical properties to generalize predictability

Examine selectivity

- Rejection of fission products (Cs, Sr, Tc)
- Other metals and anions

Demonstrate a simple flowsheet on real waste

- Choose appropriate cation exchanger
- Define conditions and contacting scheme
- Procure waste samples and run test

Future efforts using crown ethers

Advantages of using crown ethers

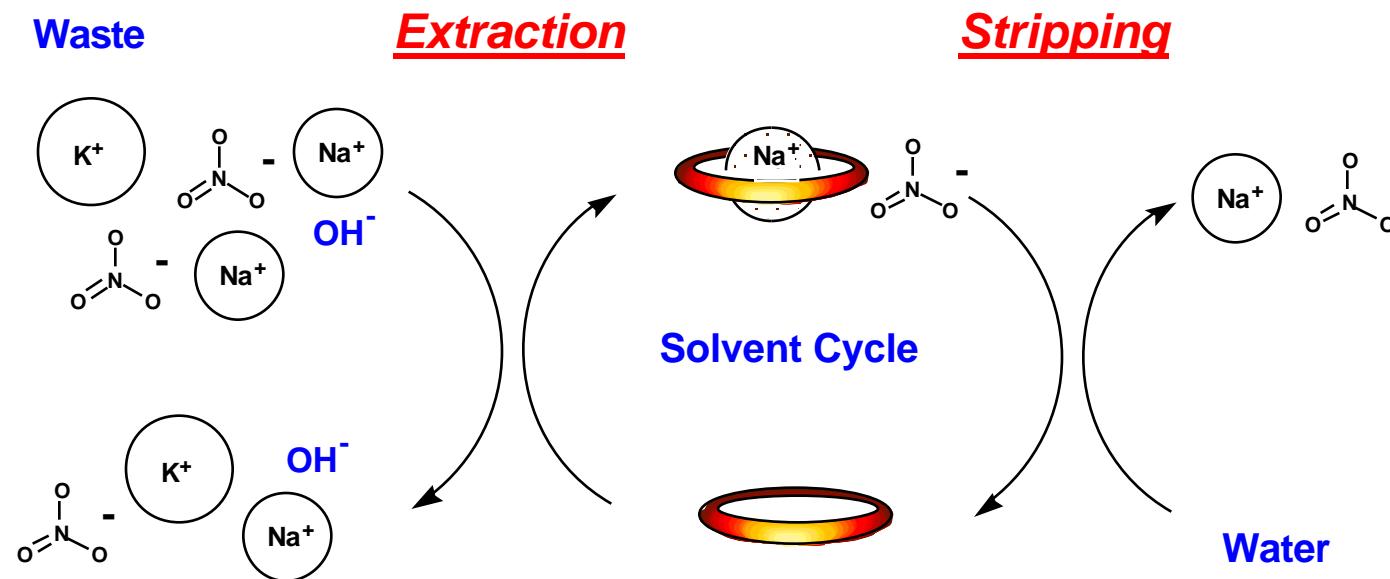
- Enhances sodium extraction strength
- Controls cation selectivity
- Lowers viscosity of loaded solvent and permit higher loading
- Expected to decrease water extraction

Main disadvantage is cost

- Extractant cost should be • \$20/gram
- Solvent recovery will likely be necessary
- Will require centrifugal contactors for high throughput

Future efforts using crown ethers

Conceptual sodium salt SX cycle:



Future efforts using crown ethers

Alternative crowns with enhanced Na^+ binding are being synthesized.

Target compounds:

Alkylated for lipophilicity and selectivity

18-Crown-6 and 16-crown-5 families

Neutral and proton-ionizable

We thank the

U.S. Department of Energy

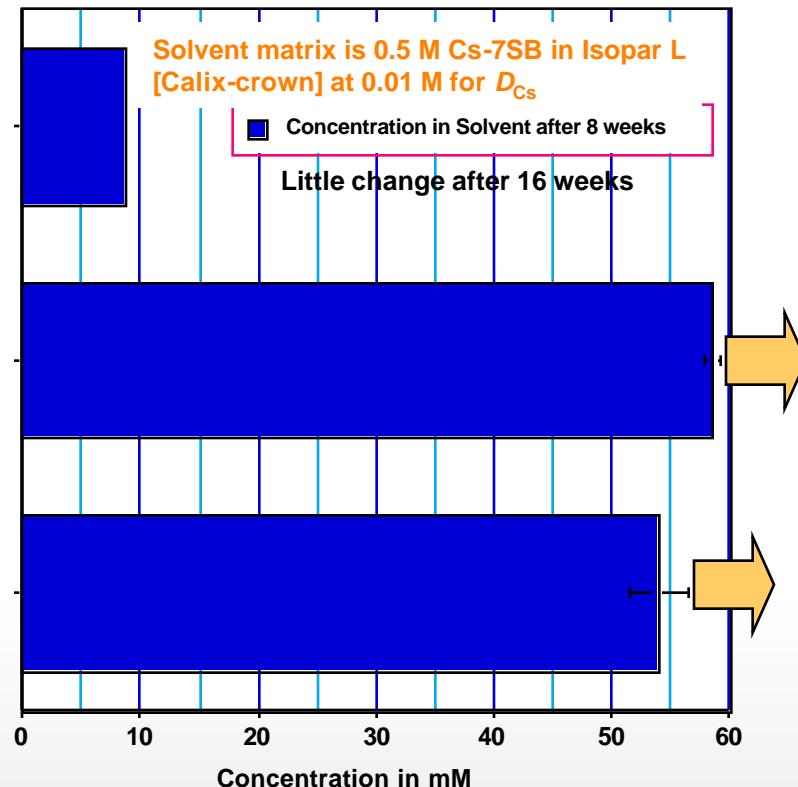
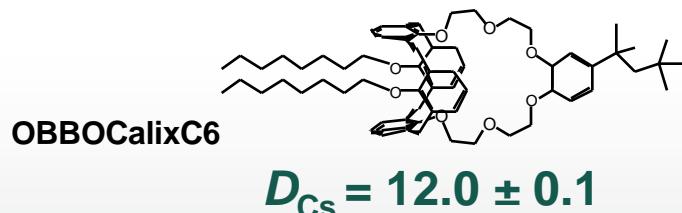
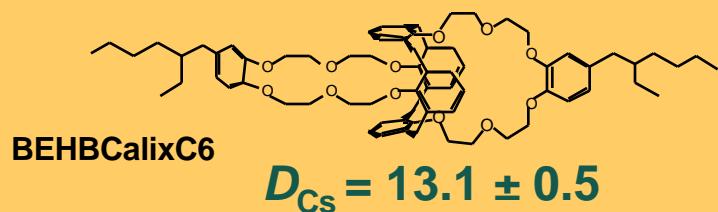
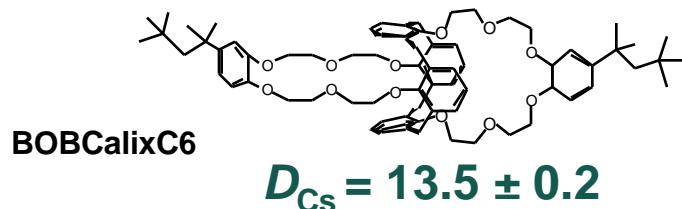
Oak Ridge National Laboratory is managed and operated by UT-Battelle, LLC,
for the U.S. Department of Energy under contract DE-AC05-00OR22725.

Pacific Northwest National Laboratory is managed and operated by Battelle Memorial
Institute for the U.S. Department of Energy under contract DE-AC06-76RLO-1830.

Highlight
Project No. 73803

New calixcrowns with high solubility and good Cs extraction strength have been synthesized

An analog of BOBCalixC6 has much higher solubility



Highlight

Project No. 73803

A highly effective alternative CSSX flowsheet
is being developed

Features improved Cs stripping and all-alkaline solutions

Solvent:

7 mM BOBCalixC6
0.75 M Cs-7SB modifier
3 mM Alkylguanidine (Lix 79)
Isopar L diluent

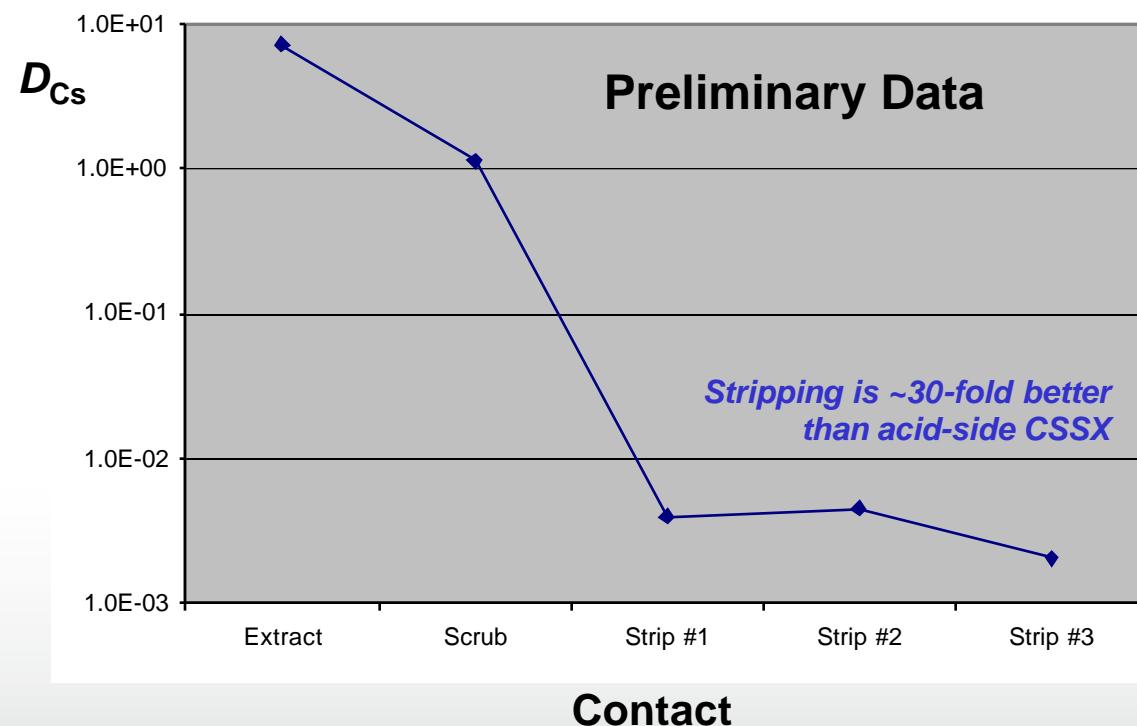
Aqueous solutions:

Extraction: 3 M NaNO₃,
2 M NaOH, 0.05 M KNO₃,
0.5 mM CsNO₃
Scrub: 0.1 M NaOH
Strip: 1 mM NaHCO₃

Conditions:

25 °C, O:A = 1:1

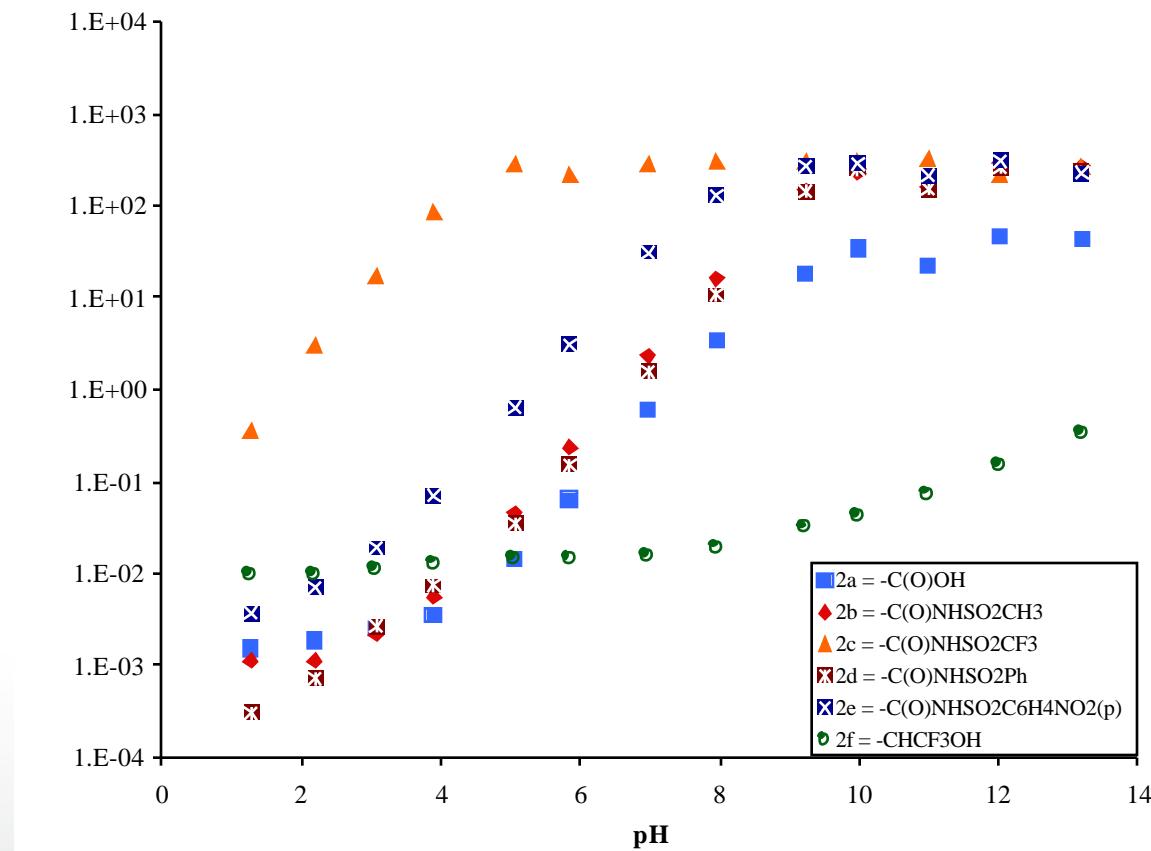
Uses CSSX solvent, with TOA replaced by an alkylguanidine



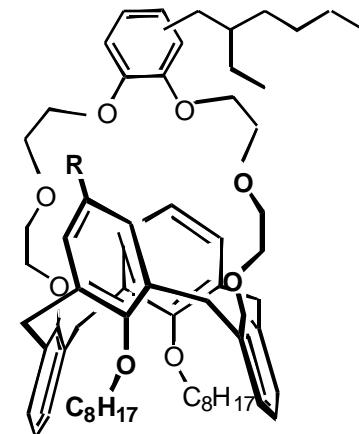
Highlight
Project No. 73803

Proton-ionizable calixcrown cesium extractants offer extremely effective cycling

Very high D_{Cs} at high pH. Very low D_{Cs} at low pH.



Compounds provided by
Prof. Richard A. Bartsch,
Texas Tech Univ.

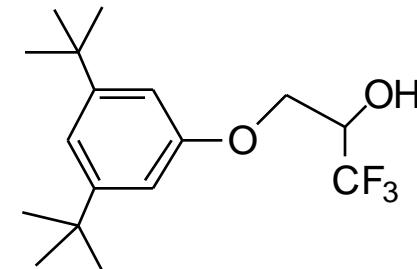
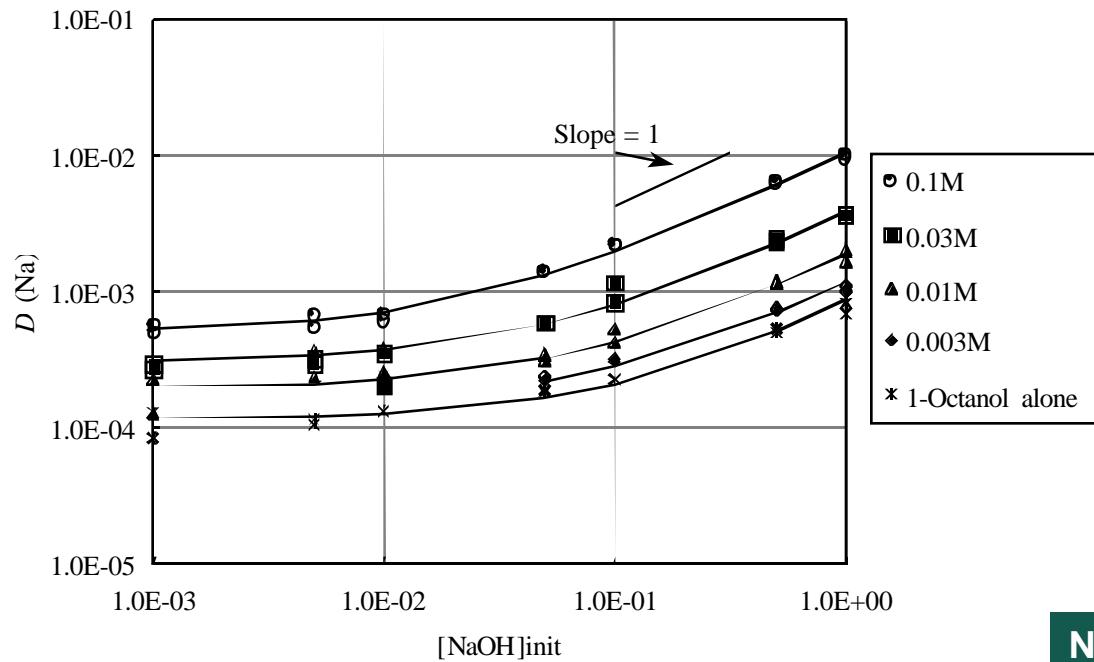


Organic phase:
10 mM calixarene in toluene
(similar results in CHCl₃)

Aqueous phase:
Buffered 0.5 M NaNO₃

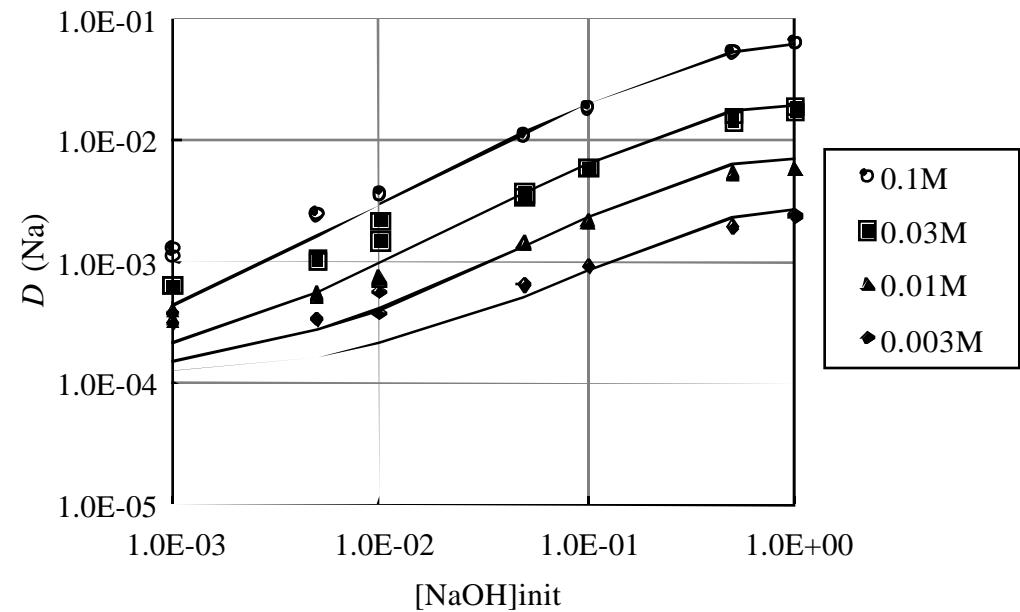
Conditions:
25 °C, O:A = 1:1

Cation-exchange model fits data



NaOH extraction isotherms
25 °C; O/A = 3
1-octanol diluent
NaOH only aqueous electrolyte

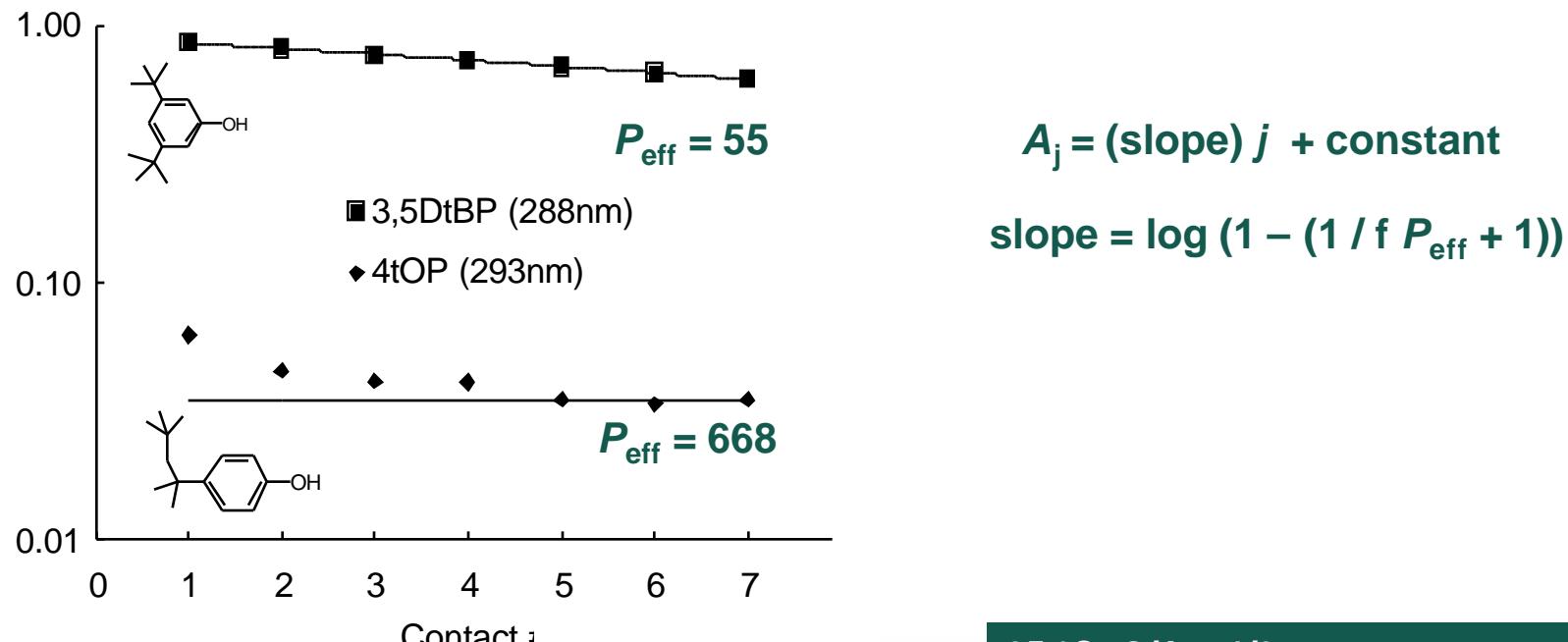
A poor fit is obtained if free ions are omitted from model



Fit assumes that 1-octanol alone can extract NaOH as free ions; otherwise fit would be even worse!

NaOH extraction isotherms
25 °C; O/A = 3
1-octanol diluent
NaOH only aqueous electrolyte

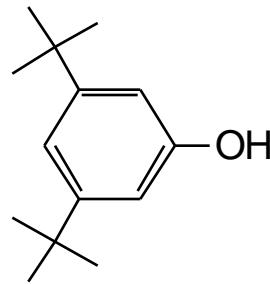
Tested alkyl phenols partition slightly from 1-octanol to 1 M NaOH



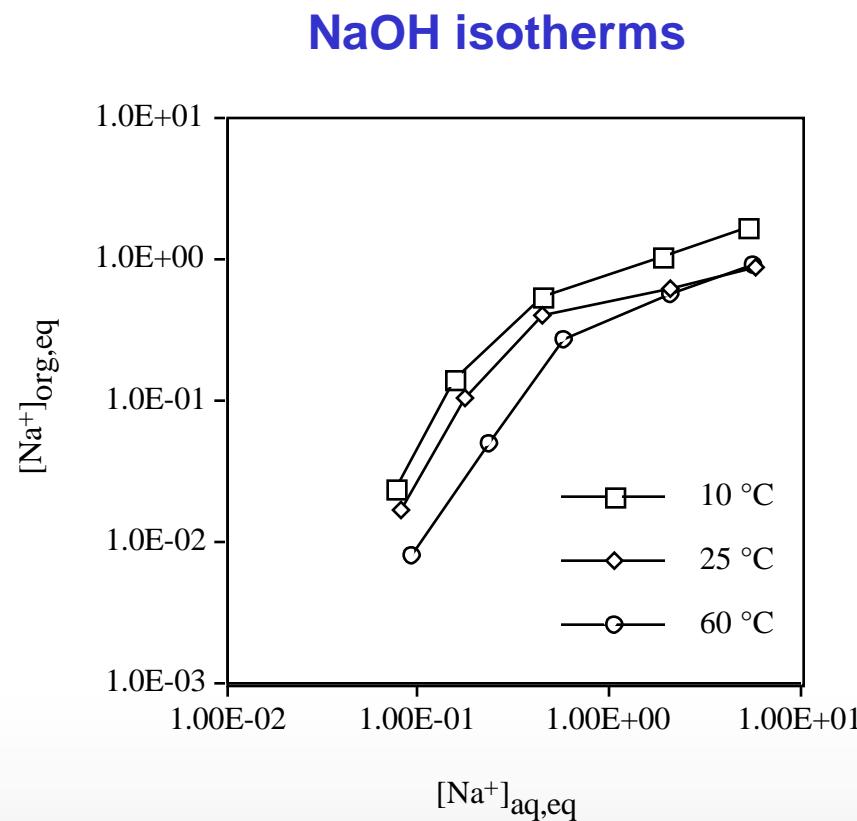
25 °C; O/A = 1/3
[Phenol]_{init,org} = 0.020 M
1-Octanol diluent
Fresh Aq. 1 M NaOH ea. contact

High loadings can be achieved over range of T

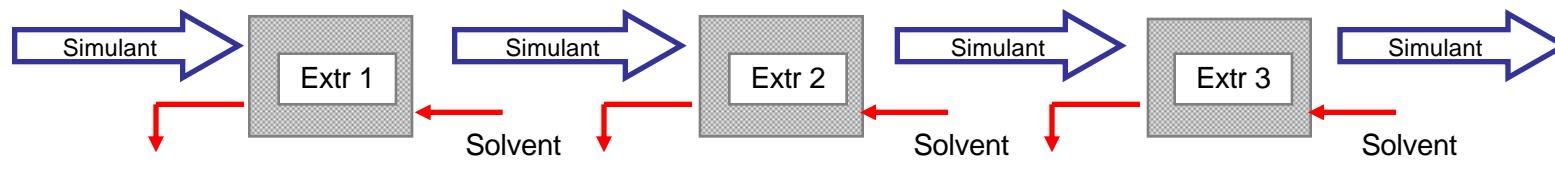
Solvent
1 M 3,5-di-*t*-butylphenol
in 1-octanol



$$\Delta H = -29 \text{ kJ}^{-1} \text{ mol}^{-1}$$
$$\Delta S = -85 \text{ J K}^{-1} \text{ mol}^{-1}$$

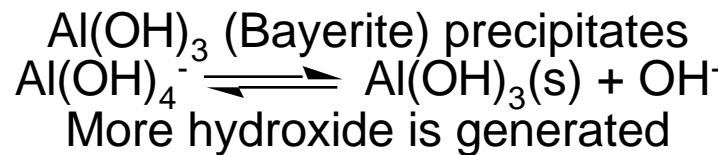


Efficient and selective NaOH removal from simulant



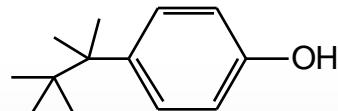
Simulant

1.88 M free NaOH
0.70 M NaAl(OH)₄
3.5 M NaNO₃



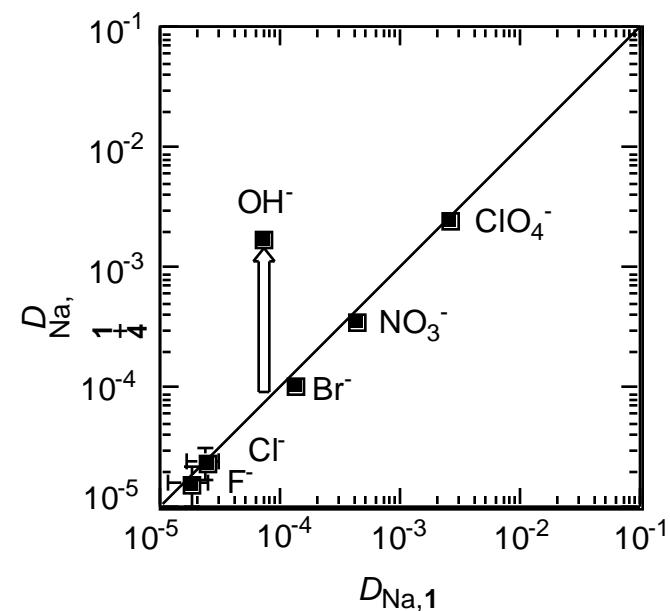
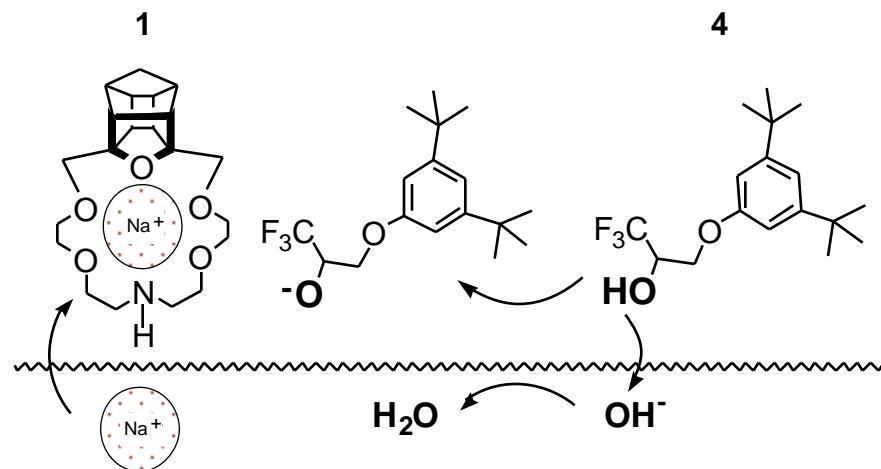
Solvent

1 M 4-*t*-octylphenol
in 1-octanol



After 3 extractions with fresh solvent @ 60 °C
107% removal of free NaOH
32% removal of Na
Avg. strip: **1.15 Na : 1 OH⁻ : 0.007 Al**

Concept of synergistic pseudo hydroxide extraction demonstrated to give selectively enhanced OH⁻ separation



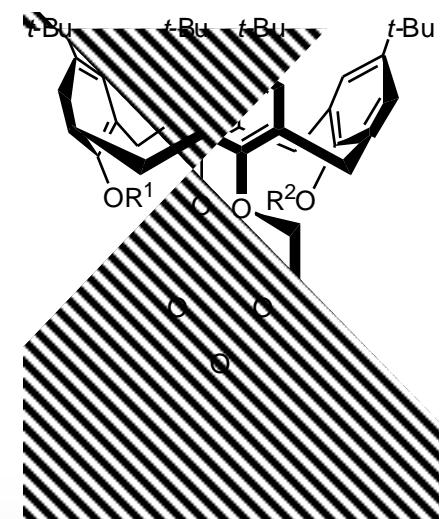
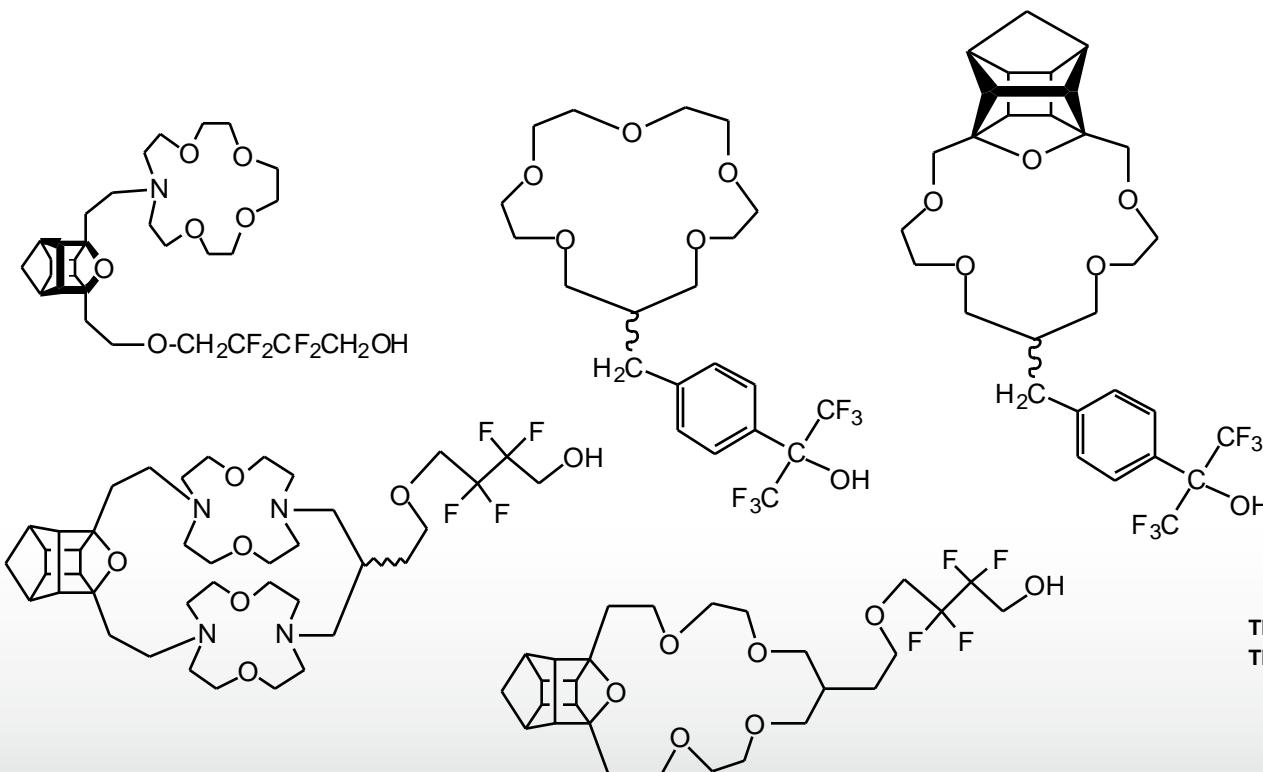
22 mM crown + 0 or 44 mM ROH in nitrobenzene; 1 M NaX in aq phase
25 °C, O/A = 1

T. G. Levitskaia, B. A. Moyer, P. V. Bonnesen, A. P. Marchand, K. Krishnudu, Z. Chen, Z. Huang, H. G. Kruger, and A. S. McKim *J. Am. Chem. Soc.* **2001**, 123, 12099–12100.

Ditopic NaOH pseudo hydroxide extractants provide insight into intra-molecular cooperativity

Synthesis by Alan P. Marchand and co-workers, Univ. of N. Texas

Lariat compounds examined:



TP-I-66 ($R^1 = R^2 = CH_2CH_2-O-CH_2CF_2CF_2CH_2OH$)
TP-1-68 ($R^1 = CH_3; R^2 = CH_2CH_2-O-CH_2CF_2CF_2CH_2OH$)

Crown ether extracts NaNO_3 with simple 1:1 mechanism that correlates with electron-pair donicity of solvent matrix

